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"Structural Characterization of Actinide – Metal Interactions in Non-crystalline Molecular Systems"

Thursday, February 14, 2002 5PM-6PM Bldg. 70A- Room 3377

Hosts: Dr. Linfeng Rao & Professor Heino Nitsche

ABSTRACT

Metal – metal interactions in molecular systems have always been a point of interest as they often lead to important physical properties. Our purpose is to better understand the actinide valence orbital behavior in non-crystalline systems and more specifically in coordination complexes of actinide which involve actinide – metal interactions. The starting point to this work aimed to characterize the metal ions coordination spheres, principally by means of X-ray Absorption Spectroscopy. Two different coordinating systems will be presented here: actinide hexacyanoferrate solid state complexes and actinide cation – cation solution complexes and related building block units.

Although a lot is known on the structure and physical properties of the transition metals and lanthanide hexacyanoferrate families, very little has been reported to date on the actinide case. We show here how the actinide hexacyanoferrates (Th to Am) compare to the lanthanide ones from a structural point of view but differ in their electronic configuration. In all cases, an actinide–cyano–iron bond (close to linear) has been characterized as a result of focussing effect in the photoelectron backscattering.

On the other hand, actinide cation - cation systems have been widely studied, mainly by means of thermodynamical or vibrational techniques (for instance RAMAN). However, the bonding mode of the two cations is still a matter of debate. Using EXAFS spectroscopy, evidences for neptunium – neptunium interactions have been looked for in the NpO_2^+/NpO_2^+ system. Additional understanding about the actinyl cation behavior has been reached by means of interpretation and simulation of their XANES spectra.